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Canulescu, Stela; Cazzaniga, Andrea Carlo; Ettlinger, Rebecca Bolt; Schou, Jørgen

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## **Non-stoichiometry in sulfides produced by pulsed laser deposition**

Stela Canulescu, Andrea Cazzaniga, Rebecca B. Ettlinger and Jørgen Schou

DTU Fotonik, Technical University of Denmark, DK-4000 Roskilde, Denmark

Pulsed laser deposition or PLD is known as a technique by which complex materials can be stoichiometrically transferred from a target to a substrate, providing that the ablation threshold is exceeded. For a multi-target component, it frequently happens that there is loss of the lightest and the most volatile component in the film. A very well studied case is the one of oxides, for which the  $O_2$  or  $N_2O$  background gases can reduce the loss of oxygen in the growing films. A much less studied case is the one of sulfides or selenides, such as the solar cell absorber layers of CIGS ( $Cu(Ga,In)Se_2$ ) and CZTS ( $Cu_2ZnSnS_4$ ). While the former material was studied comprehensively during the last thirty years as absorber layer, the latter is relatively new, promising material, which recently has reached a solar cell efficiency slightly below 10 %. Films of CZTS have turned out to be difficult to produce by PLD because the mass transfer from target to films is significantly incongruent. The films were produced by PLD at a fluence from  $0.2 \text{ J/cm}^2$  to  $2 \text{ J/cm}^2$  at room temperature with nanosecond lasers with wavelengths of 248 nm or 355 nm in vacuum. The resulting film composition was deficient in sulfur in general, but the most surprising feature was a strong decrease in the copper content of the films with decreasing fluence. There was a clear decrease of the number of droplets on the films with decreasing fluence as well. A similar trend was observed for  $Cu_2SnS_3$  or  $Cu_2ZnSn$ .